

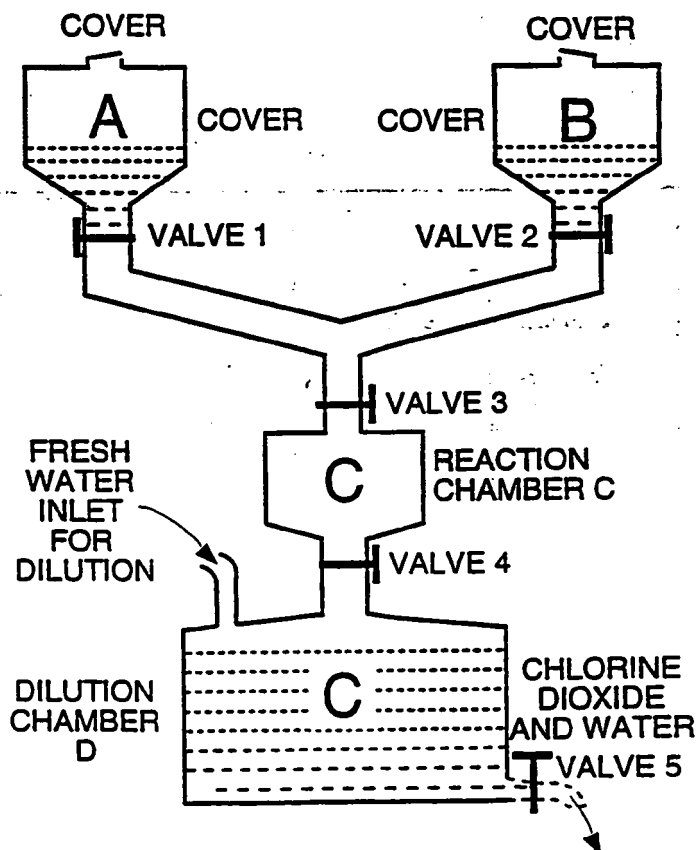


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<b>(21) International Application Number:</b> PCT/US93/02015 <b>(22) International Filing Date:</b> 4 March 1993 (04.03.93)  <b>(30) Priority data:</b> 07/846,468                      4 March 1992 (04.03.92)      US 07/980,262                      23 November 1992 (23.11.92)    US  <b>(71) Applicant:</b> ARCO RESEARCH, INC. [US/US]; 10 Ponderosa Drive, Melville, NY 11747 (US). <b>(72) Inventor:</b> ROOZDAR, Habib ; 9 Rolling Hills Drive, Nesconset, NY 11767 (US). <b>(74) Agent:</b> COLEMAN, Henry, D.; Coleman & Sudol, 261 Madison Avenue, New York, NY 10016 (US).		<b>(81) Designated States:</b> CA, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>

**(54) Title:** METHOD FOR THE PRODUCTION OF CHLORINE DIOXIDE**(57) Abstract**

The present invention relates to a method for producing chlorine dioxide ( $\text{ClO}_2$ ) disinfecting solution which preferably minimizes the amount of residual chloride ion ( $\text{ClO}_2^-$ ) so that the disinfecting solution can be used in the food, food processing, drinking water pharmaceutical production and medical and dental related industries. An additional embodiment includes chlorine dioxide generating solutions which are substantially corrosion free. In the figure, vats A and B are each stoppered so that the contents of each vat may be metered into reaction chamber C. Vat A contains chlorite and vat B contains biologically compatible acid. Vat D is the dilution chamber.



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## METHOD FOR THE PRODUCTION OF CHLORINE DIOXIDE

### Field of the Invention

The present invention relates to a method for producing chlorine dioxide ( $\text{ClO}_2$ ) disinfecting solution which preferably minimizes the amount of residual chlorite ion ( $\text{ClO}_2^-$ ) so that the disinfecting solution can be used in the food, food processing, drinking water, pharmaceutical production and medical and dental related industries.

The present invention also relates to a method for generation of chlorine dioxide ( $\text{ClO}_2$ ) in low acidity disinfecting compositions which suitable for applications where corrosion, a pH related property, is a concern and is required to be either prevented or minimized so that the disinfecting composition can be used in the treatment of metal-contaminant substrates such as dental and medical instruments and devices.

### Background of the Invention

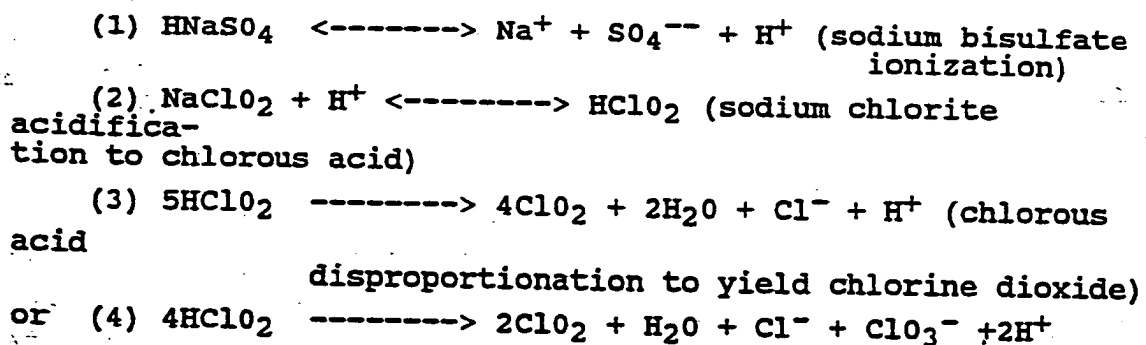
Chlorine dioxide, an indirect food additive, has been found to be especially useful as a disinfectant, antiseptic and sanitizer. It is widely used to disinfect drinking water and various water supplies. In addition, chlorine dioxide finds use as a bleaching agent for flour, fats, textiles and as an antiseptic.

Although it has great beneficial characteristics, chlorine dioxide can not be transported commercially as a concentrated gas for its use and instead has been generated at the site where it is used.

Chlorine dioxide has shown great utility as an antiseptic for treating metal substrates such as dental and medical instruments and devices. However, the prior art methods for generating chlorine dioxide suffer from the disadvantage that large quantities of chlorite remain as a residue. Chlorite residues on food handling equipment and medical and dental surfaces that are to come in contact with humans are to be avoided or substantially minimized according to FDA and EPA regulations.

Separately, chlorine dioxide exhibits certain corrosive properties which are believed to be pH related. Thus, it is beneficial to generate chlorine dioxide at a pH which would avoid or minimize corrosion during the disinfecting process.

The production of  $\text{ClO}_2$  solutions is well known in the art. The general prior art procedure has been to mix sodium chlorite ( $\text{NaClO}_2$ ) with an acid. As a rule, the stronger the acid, the faster and more efficient will be the production of chlorine dioxide. The general formula for the production of chlorine dioxide using sodium bisulfate is as follows:



According to the reaction, where a relatively strong acid is combined with sodium chlorite, the generated pool of chlorous acid is in equilibrium with the chlorite ion and not the strong acid, because the original acid is almost entirely ionized at the pH employed and hence has shifted the equilibrium toward formation of chlorous acid. In this regard, the hydrogen ion concentration from use of a relatively strong acid, as opposed to slightly ionized acids, will produce optimal concentrations of chlorous acid. In this way the generated chlorous acid has less of a tendency to ionize because the conjugate base of the original acid is not powerful enough to compete for the hydrogen ions. As a rule, the lower the pKa of the acid, less acid is needed to generate chlorous acid. When the prior art solution is evaporated from the surface of food equipment, for example, the chlorite ion either in protonated form or as the conjugate base (depending upon

pH) remains as unwanted residue.

Another requirement in the food handling and related industries is the need for raw materials or ingredients which are safe to handle in the preparation of the disinfectant. Strong acids such as nitric or hydrochloric may be dangerous to the unskilled personnel in the food handling unit and inappropriate for generating chlorine dioxide in this case. The requirement is for the inclusion of reagents which are safe to use and, after generating chlorine dioxide, produce side products which are non-toxic and/or biodegradable.

Sulfuric acid, for example, is corrosive, a powerful oxidizing agent and therefore, dangerous. Nitric acid is similar to sulfuric acid and may produce nitrosamine residues, which are carcinogenic. Hydrochloric acid is corrosive due to the chloride ion which also tends to favor the production of chlorate anion, an unfavorable result (4).

#### Objects of the Present Invention

It is an object of the present invention to provide a method for producing chlorine dioxide for use on food equipment and related surfaces including dental and medical surfaces.

It is another object of the present invention to preferably minimize the amount of residual chlorite salt in the final chlorine dioxide solution and ultimately, where applicable, on the treated surface.

It is an additional object of the present invention to provide a method for producing chlorine dioxide utilizing materials which are safe to handle.

It is a further object of the present invention to generate chlorine dioxide from chlorite and low pKa biocompatible acids.

It is still a further object of the present invention to generate chlorine dioxide from chlorite ion and minimally toxic or non-toxic (substantially non-toxic) chlorine dioxide generators which yield substantially non-toxic and/or biodegradable side products from the generation of chlorine dioxide.

It is yet another object of the present invention to generate chlorine dioxide from chlorite ion in a liquid composition utilizing non-toxic low pKa acids in which the residual levels are non-toxic.

It is yet a further object of the present invention to provide a chlorine dioxide generation method in a liquid composition containing a relatively low concentration of acid which may be used as a disinfectant having minimal corrosive properties.

These and other objects of the present invention may be readily gleaned from the description of the invention which follows.

#### Description of the Figures

Figure 1 is a diagrammatic representation of a system for producing chlorine dioxide from a salt of a chlorite and an acid, preferably a biologically compatible acid and optionally, a disproportionation agent. The reaction(s) to form chlorine dioxide occurs in the reaction chamber (C). It is noted that the pipes, chambers and vats as set forth in Figure 1 are generally made of high density polyethylene and/or polypropylene.

Figure 2 is a diagrammatic representation of a two-part system comprising two containers, one for chlorite salt and the other for the acid. In figure 2 (a and b), the two parts could be considered as two separate containers, with or without dispensing pumps. A measuring cup can be used for removing approximately equal volumes of the chlorite part and

the acid part.

### Detailed Description of the Invention

The term "salt of a chlorite" or "chlorite salt" is used throughout the specification to describe a salt of chlorite which is readily soluble in an aqueous system and which readily dissociates into chlorite anion and counterion (generally, metal). Two particularly preferred salts of chlorites for use in the present invention include sodium chlorite and potassium chlorite.

The term "low pKa acid", "non-toxic low pKa acid" "biologically compatible low pKa acid" is used throughout the specification to describe acids which are relatively strong (have pKa's of about 2.1 or lower, preferably below about 1.94, the pKa of chlorous acid so as to shift the equilibrium to chlorous acid generation) and are easily or relatively safely handled, are generally compatible with biological systems (they are substantially non-toxic) and are non-caustic. Low pKa acids donate a large fraction of hydrogen ions by favoring a reaction which consumes hydrogen ions and favors the generation of chlorine dioxide. By virtue of the low pKa, the acids utilized in the present invention are highly ionized and smaller quantities of the low pKa acid would be needed to protonate chlorite ions to form chlorous acid. Consequently, the acids have low residual levels.

The residues that are formed from these biologically compatible acids are generally the sodium and/or potassium salts of the acids, such residues being safe, non-corrosive and acceptable as either direct or indirect food additives. Examples of biologically compatible or non-toxic acids for use in the present invention include sodium and potassium bisulfate ( $\text{NaHSO}_4$  and  $\text{KHSO}_4$ ), phosphoric acid and maleic acid. The bisulfates have pKa's of about 1.9-2.0, phosphoric acid has a pKa of about 2.15 and maleic acid has a pKa of about 1.94. Other biologically compatible acids which may be used in the present invention include phosphoric acid,

ethylenediaminetetraacetic acid (EDTA, as the free acid or the monosodium salt) among others.

For purposes of the present invention, hydrochloric, nitric and concentrated sulfuric acid or sulfuric acid in its free acid form are not considered biologically compatible acids for purposes of the present invention because of their caustic nature and their resultant difficulty in handling. However, in certain embodiments according to the present invention, especially including those embodiments which include a disproportionation agent, these acids may be used, preferably in diluted form.

The term "chlorous acid disproportionation agent", "disproportionation agent" or "aldehyde agent" is used throughout the specification to describe a number of disproportionation agents which enhance the rate of disproportionation of chlorous acid to produce significantly increase the amount of chlorine dioxide which is produced and minimizes residual chlorite ion. The disproportionation agents according to the present invention are chosen for their ability to substantially enhance the rate and efficiency (yield) at which chlorine dioxide is formed from chlorous acid (even at relatively high pH's and low concentrations of acid--a consideration in the embodiments which minimize corrosion), for their ability to form their biologically compatible substantially non-toxic organic acid side products and for their ability to minimize residual chlorite ion. Thus, by using a disproportionation agent according to the present invention, one can produce effective quantities of  $\text{ClO}_2$ , minimize the amount of acid used, raise the pH of the  $\text{ClO}_2$ -generating solution to a non-corrosive level, if desired,

Disproportionation agents for use in the present invention include, for example, substantially non-toxic aldehydes such as acetaldehyde, benzaldehyde, glutaraldehyde, cinnamic aldehyde, propionaldehyde, paraldehyde, 2-Furfural (bran oil) and 5-Hydroxymethyl-2-furfural (5HMF), among others. Preferred disproportionation agents for use in the



present invention include those aldehydes that are substantially non-toxic themselves and which are converted during the disproportionation process to substantially non-toxic side products. Acetaldehyde, benzaldehyde, cinnamic aldehyde, glutaraldehyde and propionaldehyde are particularly preferred for use in the present invention.

The term "corrosive properties" is used throughout the specification to describe properties such as those producing corrosion on metal substrates such as medical and/or dental devices. These properties are derived from factors such as excess residual acidity (low pH) and/or excess residual chlorite ion.

The term "enhanced chlorous acid disproportionation" is used throughout the specification to describe the production of chlorine dioxide from chlorous acid in the presence of a disproportionation agent such as an aldehyde, a combination which has a faster rate and greater efficiency of chlorite ion use even when the pH is less acidic and which generally produces chlorine dioxide in greater amounts and at higher concentrations than without a disproportionation agent. In general, in the absence of a disproportionation agent, the amount of chlorine dioxide which is generated in a reaction at a pH of about 3.9 during a 15 minute period is generally no greater than about 1-2 parts per million. This indicates that the rate of conversion of chlorous acid to chlorine dioxide in this case is very slow and the yields are low. In addition, residual acid remains, thus increasing the potential for producing corrosion.

Utilizing a disproportionation agent in the form of an aldehyde at the same starting pH of 3.9, the amount of chlorine dioxide generated may be as much as about 40 ppm or more. In this case, hydrogen ions and residual chlorite ions are consumed by the disproportionation of chlorous acid, such that at the end of a 15 minute period, the pH rises to about 4.3. This more efficient process for producing chlorine dioxide results in chlorite ion levels being substantially

reduced relative to processes which generate chlorine dioxide in the absence of an aldehyde. In preferred embodiments according to the present invention, at the end of the 15-minute period, the residual chlorite ion levels are about 60% or less of the initial chlorite ion.

The terms "minimize residual chlorite ion", "minimizing residual chlorite ion" or "substantially reduce residual chlorite ion" are used throughout the specification to describe reactions to produce chlorine dioxide which yield no more than about 85% by weight residual chlorite ion (based upon the initial weight of chlorite used). Preferably, the amount of residual chlorite ion is less than about 70% by weight and most preferably the amount of residual chlorite ion is less than about 60% by weight.

The term "substantially non-toxic" is used throughout the specification to describe disproportionation agents and/or biologically compatible acids which are used to generate chlorine dioxide in the method(s) according to the present invention. Substantially non-toxic means that the materials are safely handled and are generally compatible with biological systems in amounts used to generate chlorine dioxide relative to compositions which are considered "substantially toxic." The term "substantially" is used to describe the non-toxic acids and disproportionation agents for use in the present invention because of the fact that almost all substances, including water, may become toxic to a biological system in certain amounts.

The term "substantial quantity" is used to describe amounts of chlorine dioxide which are produced using the method according to the present invention and are believed to be useful. A substantial quantity of chlorine dioxide for purposes of the present invention is at least about 1 part per million, because chlorine dioxide is a disinfectant at that concentration and higher concentrations. In the present invention chlorine dioxide is preferably produced in a concentration of at least about 5 parts per million, most

preferably at least about 20-40 parts per million.

The terms "low acidity composition" and "high pH acid composition" are used throughout the disclosure to describe a chlorine dioxide-generating composition (producing at least about 1 ppm chlorine dioxide) and having a relatively low concentration of acid to produce an initial pH of about 3.5 to about 4.5, and which comprises an amount of a water soluble salt of chlorite with an amount of a low pKa acid effective to produce a pH within the above range. The composition may be dry or in solution.

The term "chlorite part" is used throughout the specification to describe the form in which an amount of a water soluble salt of chlorite either in dry or liquid state is added to the acid part.

The term "acid part" is used throughout the specification to describe the form in which an amount of a water soluble low pKa acid either in dry or liquid state is added to the chlorite part.

The term "low acidity condition" is used throughout the specification to describe the condition at which at least 1 part per million (ppm) of chlorine dioxide is generated in a solution with a starting pH ranging from about 3.5 to about 4.5. This condition is provided by combining an effective amount of a low pKa acid with an amount of a water soluble salt of chlorite. The overall pH for purposes of the present invention will preferably range from about 2 to about 4.5.

The term "effective amount" is used throughout the specification to describe a minimum amount or quantity of a component, i.e., a low pKa acid, disproportionation agent or chlorite ion included to generate an intended effect. The term effective amount when used to describe the low pKa acid, is used to describe that amount of acid, either in dry or liquid form which, when combined with chlorite in solution will generate at least 1 part per million (ppm) of chlorine dioxide

from chlorous acid. By definition, 1 part per million is equal to 0.0001% by weight.

The present invention relates to a method of producing chlorine dioxide comprising:

- 1) combining an amount of a salt of chlorite with an amount of a low pKa biologically compatible acid effective to produce a substantial quantity of chlorous acid, said chlorous acid disproportionating to form chlorine dioxide. This method reduces the amount of residual chlorite ion relative to prior art methods and is compatible with food, medical device and dental surfaces. This method may be performed at an initial pH no greater than about 4.5. In embodiments according to the present invention, substantial corrosion resistance is instilled by utilizing an initial pH of about 3.5 to about 4.5.

The present invention also relates to a method of producing chlorine dioxide comprising:

- 1) combining an amount of a salt of chlorite with an amount of an acid, preferably a low pKa biologically compatible acid effective to produce a substantial quantity of chlorous acid; and

- 2) providing an amount of a disproportionation agent in the form of aldehyde chemical entity effective to enhance chlorous acid disproportionation to chlorine dioxide, said disproportionation agent giving rise to a substantially non-toxic organic acid and/or organic acid salt side products. Such a method of generating chlorine dioxide will generally minimize the residual chlorite ion by providing for a more efficient disproportionation of chlorous acid. In the method according to the present invention which provides substantial corrosion resistance, lower concentrations of a low pKa acid and chlorite are used compared to prior art methods, further diminishing the residual chlorite ion.

In the first method according to the present invention, an effective amount of a salt of a chlorite, preferably sodium or potassium chlorite is combined with a biologically

compatible acid to produce a substantial quantity of chlorous acid. In a second step, the chlorous acid produced is allowed to disproportionate to form chlorine dioxide.

In the first method according to the present invention, preferred salts of chlorites include sodium and potassium chlorite. The biologically compatible acids according to the present invention are those acids which are generally considered safe, user friendly and substantially non-toxic, for example salts of bisulfate, maleic acid and phosphoric acid, among others. Generally, the concentration of chlorite salt used to generate chlorous acid in the present invention represents at least about 0.0005M and preferably ranges from about 0.002M to about 0.5M or slightly higher. In the embodiments which are substantially non-corrosive, the amount of chlorite salt comprises at least about 0.0005M and preferably ranges from about 0.002M to about 0.2M.

The amount of acid, preferably biologically compatible acid, added to the chlorite salt is generally that amount effective to provide an initial pH of the reaction mixture below about 4.5, preferably lower than about 3.5 or less. In embodiments according to the present invention where corrosion resistance is not important, preferably, as a rule of thumb, the low pKa acid is added in an amount which will render the initial pH in the reaction chamber, i.e., in the presence of chlorite ion, to a level below about 2.5 and most preferably to a level at or below about 2.2. In embodiments according to the present invention in which the corrosion resistance is desired, the initial pH generally ranges from about 3.5 to about 4.5. The acid is generally provided in a concentration of about 0.00005M to upwards of about 1M, depending upon the final pH of the solution desired. In corrosion resistant compositions, the concentration of acid preferably ranges from about 0.01M to about 0.2M, depending upon the amount of chlorite in the composition. In compositions in which having the characteristic of corrosion resistance is not important, the amount of acid preferably ranges from about 0.01M to upwards of 1M or more. These concentrations will generally

provide a pH of less than about 2.5 and usually less than about 2.0. Concentrations of acid producing pH's above or below these values may also be used, depending upon the amount of chlorite to be converted to chlorine dioxide, as well as the pH desired in the reaction chamber and the ultimate concentration of chlorine dioxide desired.

In the first method according to the present invention, the chlorite salt is combined with the acid at about 15°C to about 30°C to produce chlorous acid. Thereafter, the chlorous acid is left to disproportionate to chlorine dioxide. In general, the disproportionation step is carried out in the same aqueous medium where the formation of chlorous acid occurs. The temperature of the disproportionation step may vary, but will generally range from about 15°C to about 30°C or higher. After production, the chlorine dioxide solution may be used directly or diluted depending upon the desired use.

In a second method according to the present invention, the use of a disproportionation agent, preferably in the form of an aldehyde chemical entity, will enhance and hasten the production of chlorine dioxide from chlorous acid. In this aspect of the present invention, either during or after the formation of chlorous acid, an effective amount of an agent for disproportionating chlorous acid to chlorine dioxide is added to the solution. While the disproportionation agent may be added after the formation of chlorous acid, preferably the disproportionation agent is already present in the acid solution when the acid solution is combined with the aqueous mixture of chlorite salt. In this way, as soon as chlorous acid is generated, the disproportionation reaction may be enhanced. The overall result will be to shift the equilibrium toward more chlorous acid generation and consequently, more chlorine dioxide formation. Using a disproportionation agent, at least 10% and generally at least about 30-40% up to about 80% or higher of chlorite ion is converted to chlorine dioxide and chloride ion. In the absence of a disproportionation agent such as an aldehyde disproportionation agent, the conversion

is significantly slower and is less efficient (usually significantly less than about 2% of the initial chlorite ion is converted to chlorine dioxide and/or chloride).

It is noted that in this aspect of the present invention which utilizes a disproportionation agent to enhance chlorous acid disproportionation to form chlorine dioxide and minimize residual chlorite, any acid which produces an initial pH in the reaction mixture of about 4.5 or lower may be utilized, but preferably a low pKa biologically compatible acid is used.

In general, the amount of disproportionation agent used in the present invention varies depending upon the amount of chlorite ion used. In general, the amount of disproportionation agents used in the present invention ranges from about 10 parts per million to about 20,000 parts per million or more (about 0.001% to about 2.0% by weight). In general, on a mole to mole basis, the amount of disproportionation agent utilized varies from about 1/10 to about 1/2 the amount of chlorite used, and preferably about 1/3 to about 1/2. While it is possible to utilize a disproportionation agent in concentrations above and below this amount, for example, it is noted that at concentrations of disproportionation agent substantially below 1/10 the molar concentration of chlorite, the rate at which disproportionation of chlorous acid to chlorine dioxide occurs may be diminished. At molar concentrations of disproportionation agent significantly above about 1/2 the concentration of chlorite, residual amounts of disproportionation agent may remain in solution which could result in instability in the resulting chlorine dioxide solution. The amount of disproportionation agent is chosen to maximize chlorine dioxide formation and minimize the amount of residual chlorite in the chlorine dioxide mixture.

In the method according to the present invention, the apparatus as set forth in figures 1 and 2A and 2B are representative of systems that can be used to generate chlorine dioxide. As set forth in figure 1, a chosen amount of

chlorite salt is dissolved in water in vat A. Preferably, the chlorite salt is the sodium or potassium salt. The concentration of chlorite salt chosen generally ranges from about 0.001 to about 0.5 Molar (generally, for example, about 0.09g. to about 45g./liter of sodium chlorite). The chlorite salt is first added to water and dissolved. Depending upon the type and final concentration of chlorite chosen, the pH of the solution in Vat A may range from about 9.0 to significantly above about 10. A pH above 10, for example about 10.5, is often employed.

A second solution, contained in Vat B, is prepared containing an effective amount of a biologically compatible acid, for example, sodium bisulfate. In embodiments according to the present invention in which corrosion is not a concern, the pH of the solution without disproportionation agent is preferably maintained below about 2.5. The amount of acid chosen is that amount which is effective to produce a substantial quantity of chlorous acid. This amount of acid will generally provide an initial pH of the reaction mixture in which chlorine dioxide is produced below about pH 2.5. Optionally, into this acid solution, an effective amount of a disproportionation agent may be added to enhance disproportionation of chlorous acid to chlorine dioxide. The final pH of the acid solution including disproportionation agent in this aspect of the invention is generally less than about 2.5, preferably less than about 2.0 and most preferably less than about 1.8. In this aspect of the present invention which includes a disproportionation agent, any acid may be used including any of the aforementioned acids, among others, but preferably a low pKa biologically compatible acid is chosen.

Vats A and B are each stoppered so that the contents of each vat may be metered into reaction chamber C. Each or both of the Vats may be graduated. The stoppering of vats A and B (valves (1) and (2)) will allow a measured or pre-measured amount of the contents of each Vat to be delivered in a controllable manner to the reaction chamber C while valve



(3) is open and (4) is closed. In the reaction chamber, the chlorite is acidified with the low pKa biologically compatible acid to produce chlorous acid and subsequently, the generated chlorous acid is disproportionated in situ into chlorine dioxide. The concentration of chlorine dioxide increases within the reaction chamber until such time as the reaction is completed. In general, the reaction(s) to produce chlorine dioxide without the aid of the disproportionation agent is slow and may require about 30 minutes or higher to be completed (level off).

With an effective amount of disproportionation agent, the concentration of chlorine dioxide generated within a period of about 15 minutes ranges from about 5 ppm to upwards of 100 ppm or more. The production of chlorine dioxide may be monitored photometrically at 360 nm using an extinction coefficient of  $1250 \text{ M}^{-1}\text{cm}^{-1}$  as described on pp.244-245 of "Chemistry of Chlorine Dioxide", In Progress in Inorganic Chemistry, Vol. 15, S.J. Lippard (Editor), Wiley-Interscience, New York (1972). In the present invention, in general, the final concentration of chlorine dioxide in the reaction chamber ranges from about 80-100 parts per million (ppm) to upwards of 400 ppm.

After the completion of the formation of chlorine dioxide in reaction chamber C, the contents of reaction chamber C are deposited into dilution tank D by opening valve 4 (valve 5 is closed). Here, the chlorine dioxide solution from reaction chamber C is mixed with water or other aqueous solution in dilution tank D (generally about a 20-40 fold dilution, preferably about 30 fold) so as to create a chlorine dioxide solution with a final concentration generally ranging from slightly less than about 1 ppm to about 10 ppm, with a preferred concentration of about 1 ppm to about 5 ppm. The pH of the final diluted solution of chlorine dioxide ranges from about 4.5 to about 7 with a preferred range from about 5.5 to about 6.5.

In figures 2A and 2B, which figures are representative

of the non-corrosive aspect of the instant invention, the chlorite part ranges from about 50 ppm to about 50,000 ppm. The pH of the chlorite part may generally range from about 9.0 to about 10.8. The acid part contains an effective amount of a low pKa acid, preferably non-toxic, the pH of the concentration ranging from about 3.5 to about 4.5. Into the acid part, optionally, may be added an amount of an aldehyde disproportionation agent effective to enhance disproportionation of chlorous acid to chlorine dioxide. The amount of aldehyde disproportionation agent ranges from about 20 ppm to about 40,000 ppm. In this aspect of the present invention in which the aldehyde disproportionation agent is utilized, any acid may be used including any of the aforementioned acids, among others, but preferably a non-toxic low pKa acid is used.

The final solutions of chlorine dioxide in diluted form may be used for purposes of disinfecting surfaces, especially surfaces which may require reduced amounts of chlorite ion, for example, food equipment, and medical devices and dental equipment. In addition, the solutions according to the present invention may also be used for any other known purpose especially including for drinking water. The number of applications of the chlorine dioxide solutions according to the present invention is believed to be larger than for solutions which are produced according to prior art methods because the solutions of the instant invention are compatible with food, medical and dental equipment as well as other uses known in the art.

#### EXAMPLES

The following examples are provided to illustrate the present invention and should not be construed to limit the scope of the invention of the present application in any way.

##### Example 1

To Vat A (See Figure 1) was added an aqueous solution containing about 0.7g./liter of pure sodium chlorite (T.R.-AMC

Chemicals, a Division of TR-Metro Chemicals, Inc., Ridgefield, New Jersey). To Vat B was added about 0.4 g./liter of potassium bisulfate, which produced a pH of about 1.9. To this solution about 0.2g/liter of acetaldehyde was added.

The contents of Vat A and Vat B were emptied into the reaction chamber C by opening valves 1, 2 and 3 (valve 4 is closed). The pH of the mixture in the reaction chamber is approximately 2.2. The reaction mixture was allowed to stand for a period of ten minutes after which time approximately 92% of the initial chlorite salt had been converted to chlorine dioxide (40%) and chloride ion (60%). The concentration of chlorine dioxide in the aqueous solution in the reaction chamber was about 110 ppm as measured spectrophotometrically at 360 nm using an extinction coefficient of  $1250 \text{ M}^{-1}\text{cm}^{-1}$ . The concentration of chlorite ion which remains was approximately 30 ppm. The concentrated chlorine dioxide solution is thereafter delivered to the dilution tank D and diluted 30 fold to a final concentration of 3.5 ppm chlorine dioxide and a pH of about 6. In the final diluted disinfectant solution, the concentration of chlorite ion is about 1 or less ppm. The relatively high pH of the solution is caused by the 30-fold dilution, the production of water using up hydronium ( $\text{H}_3\text{O}^+$ ) ions during the reaction and the effect of chlorine dioxide as a Lewis Acid is minimized at high dilution.

#### Example 2

Same method employed as in example 1, except that into Vat B was added 0.4 g/liter of potassium bisulfate in combination with 0.18g/liter of propionaldehyde. The resulting solution produced a concentration of chlorine dioxide of about 110 ppm in the reaction chamber C as measured spectrophotometrically at 360 nm using an extinction coefficient of  $1250 \text{ M}^{-1}\text{cm}^{-1}$ . A 30 fold dilution of the final concentration of chlorine dioxide produced a final concentration in the dilution chamber D of about 3.5 ppm chlorine dioxide and a final concentration of chlorite ion of about 1 or less ppm.

### Example 3

Same method employed as in example 1, except that into Vat B was added 0.4 g/liter of potassium bisulfate in combination with about 0.29g/liter of benzaldehyde. The resulting solution produced a concentration of chlorine dioxide of about 30-40 ppm in the reaction chamber C as measured spectrophotometrically at 360 nm using an extinction coefficient of  $1250 \text{ M}^{-1}\text{cm}^{-1}$ . A 30 fold dilution of the final concentration of chlorine dioxide produced a final concentration in the dilution chamber D of about 1.0 ppm chlorine dioxide and a final concentration of chlorite ion which is significantly less than if disproportionation had not been included.

### Example 4

In an embodiment related to the non-corrosive aspect according to the present invention, as in Example 1, the following two-part formulation when combined in about a 1:1 ratio provides a composition useful for the disinfection of hard substrates such as dental and/or medical devices.

#### Liquid Disinfectant

<u>Chlorite Part</u> <u>Weight</u>	<u>Percent by</u>
Sodium chlorite (80%)	0.250%
EDTA, tetra sodium (98%)	0.095%
Sodium lauryl sulfate	0.004%
Deionized Water	q.s.
<u>Acid Part</u>	
Potassium bisulfate (anhydrous)	0.400%
Sodium propionate	0.150%
Glutaraldehyde (50%)	0.080%
Cinnamic aldehyde	0.015%
Deionized Water	q.s.

As noted, the disproportionation agent in the form of an aldehyde entity, namely glutaraldehyde, is preferably added to the acid part. In this example, cinnamic aldehyde is used as a fragrance. The resulting composition after 15 minutes

has a pH of about 4.2 and produces a concentration of chlorine dioxide of about 45 ppm as measured spectrophotometrically at 360 nm (molar absorptivity of 1250 per mole/centimeter). Within this period, about 40% of the initial chlorite is consumed. This composition is readily applicable for disinfection of hard surfaces such as dental and/or medical devices.

#### Example 5

In a preferred composition related to the non-corrosive aspect of the present invention, which results from about a 1:1 ratio of a combination of the following two part formulation, a liquid disinfectant is obtained which is useful for applications on dental and/or medical devices.

#### Liquid Disinfectant

##### Chlorite Part

Sodium chlorite (80%)  
EDTA, tetra sodium (98%)  
Sodium lauryl sulfate  
Deionized Water

##### Percent by

0.250%  
0.095%  
0.004%  
q.s.

##### Acid Part

Potassium bisulfate (anhydrous)  
Sodium propionate  
Propionaldehyde  
Deionized Water

0.360%  
0.150%  
0.010%  
q.s.

As noted, the disproportionation agent in the form of an aldehyde entity, namely propionaldehyde, is preferably added to the acid part. The resulting composition has a pH of about 3.9 and produces a concentration of chlorine dioxide of about 38 ppm as measured spectrophotometrically at 360 nm (molar absorptivity of 1250 per mole/centimeter during a period of about 10 minutes. Within this period, about 15% of the initial chlorite is consumed. This composition is readily applicable for disinfection of hard surfaces such as dental and/or medical devices.

#### Example 6

In yet another embodiment related to the non-corrosive aspect according to the present invention, the following two-part formulation when combined in about a 1:1 ratio provides a composition useful for the disinfection of hard substrates such as dental and/or medical devices. The pH of the composition is about 4.2 and produces about 27 ppm of chlorine dioxide during an aging period of about 15 minutes.

Liquid Disinfectant

<u>Chlorite Part</u> <u>Weight</u>	<u>Percent by</u>
Sodium chlorite (80%)	0.190%
EDTA, tetra sodium (98%)	0.092%
Sodium lauryl sulfate	0.004%
Deionized Water	q.s.
<u>Acid Part</u>	
Potassium bisulfate (anhydrous)	0.300%
Sodium propionate	0.150%
Propionaldehyde	0.030%
Deionized Water	q.s.

This invention has been described in terms of specific embodiments set forth in detail herein, but it should be understood that these are by way of illustration and the invention is not necessarily limited thereto. Modifications and variations will be apparent from the disclosure and may be resorted to without departing from the spirit of the inventions those of skill in the art will readily understand. Accordingly, such variations and modifications are considered to be within the purview and scope of the invention and the following claims.

**Claims:**

1. A method of producing chlorine dioxide comprising:
  - 1) combining an amount of a salt of chlorite in solution with an amount of a low pKa biologically compatible acid effective to produce a substantial quantity of chlorous acid from chlorite ion; and
  - 2) providing an amount of a disproportionation agent in said solution effective to enhance chlorous acid disproportionation to chlorine dioxide.
2. The method according to claim 1 wherein said disproportionation agent gives rise to a substantially non-toxic side product.
3. The method according to claim 1 wherein said biologically compatible acid is selected from the group consisting of an aqueous soluble salt of bisulfate, maleic acid, phosphoric acid, ethylenediaminetetraacetic acid and monosodium ethylenediaminetetraacetic acid.
4. The method according to claim 3 wherein said bisulfate salt is sodium or potassium bisulfite.
5. The method according to claim 1 wherein said salt of chlorite is sodium or potassium chlorite.
6. The method according to claim 1 wherein said disproportionation agent is selected from the group consisting of glutaraldehyde, acetaldehyde, benzaldehyde, propionaldehyde, cinnamic aldehyde, 2-furfural and 5-hydroxymethyl-2-furfural.
7. The method according to claim 1 wherein said disproportionation agent is selected from the group consisting of glutaraldehyde, acetaldehyde, cinnamic aldehyde, benzaldehyde and propionaldehyde.
8. A method of producing chlorine dioxide comprising:
  - 1) combining an amount of a salt of chlorite in solu-

tion with an amount of a low pKa biologically compatible acid effective to produce a substantial quantity of chlorous acid from chlorite ion; and

2) providing an amount of a disproportionation agent in the form of an aldehyde in said solution effective to enhance disproportionation of chlorous acid to chlorine dioxide, said disproportionation agent giving rise to an organic acid or organic acid salt side product.

9. The method according to claim 8 wherein said disproportionation agent minimizes the amount of residual chlorite ion.

10. The method according to claim 8 wherein said biologically compatible acid is selected from the group consisting of an aqueous soluble salt of bisulfate, maleic acid, phosphoric acid, ethylenediaminetetraacetic acid and monosodium ethylenediaminetetraacetic acid.

11. The method according to claim 10 wherein said bisulfate salt is sodium or potassium bisulfate.

12. The method according to claim 8 wherein said salt of chlorite is sodium or potassium chlorite.

13. The method according to claim 8 wherein said disproportionation agent is selected from the group consisting of glutaraldehyde, cinnamic aldehyde, acetaldehyde, benzaldehyde, propionaldehyde, 2-furfural and 5-hydroxymethyl-2-furfural.

14. The method according to claim 13 wherein said disproportionation agent is selected from the group consisting of glutaraldehyde, cinnamic aldehyde, acetaldehyde, benzaldehyde and propionaldehyde.

15. A chlorine dioxide generating composition comprising:

1) an amount of a salt of chlorite in solution in combination with an amount of a low pKa biologically compatible acid effective to produce a substantial quantity of chlorous



acid from chlorite ion; and

2) an amount of a disproportionation agent in the form of an aldehyde in said solution effective to enhance disproportionation of chlorous acid to chlorine dioxide, said disproportionation agent giving rise to an organic acid or organic acid salt side product.

16. The composition according to claim 15 wherein said biologically compatible acid is selected from the group consisting of an aqueous soluble salt of bisulfate, maleic acid, phosphoric acid, ethylenediaminetetraacetic acid and monosodium ethylenediaminetetraacetic acid.

17. The composition according to claim 16 wherein said bisulfate salt is sodium or potassium bisulfate.

18. The composition according to claim 15 wherein said salt of chlorite is sodium or potassium chlorite.

19. The composition according to claim 15 wherein said disproportionation agent is selected from the group consisting of glutaraldehyde, cinnamic aldehyde, acetaldehyde, benzaldehyde, propionaldehyde, 2-furfural and 5-hydroxymethyl-2-furfural.

20. The composition according to claim 19 wherein said disproportionation agent is selected from the group consisting of glutaraldehyde, cinnamic aldehyde, acetaldehyde, benzaldehyde and propionaldehyde.

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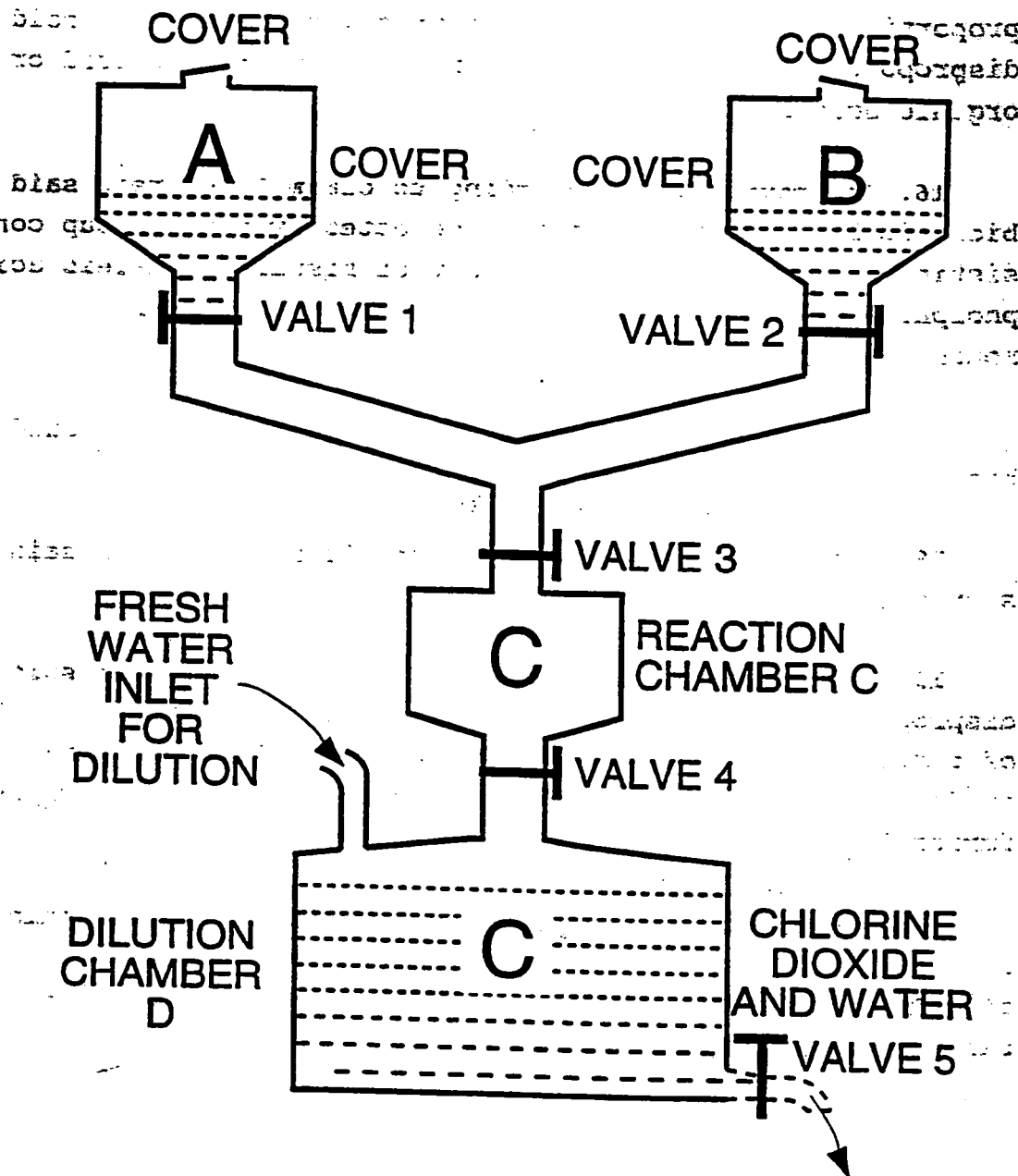
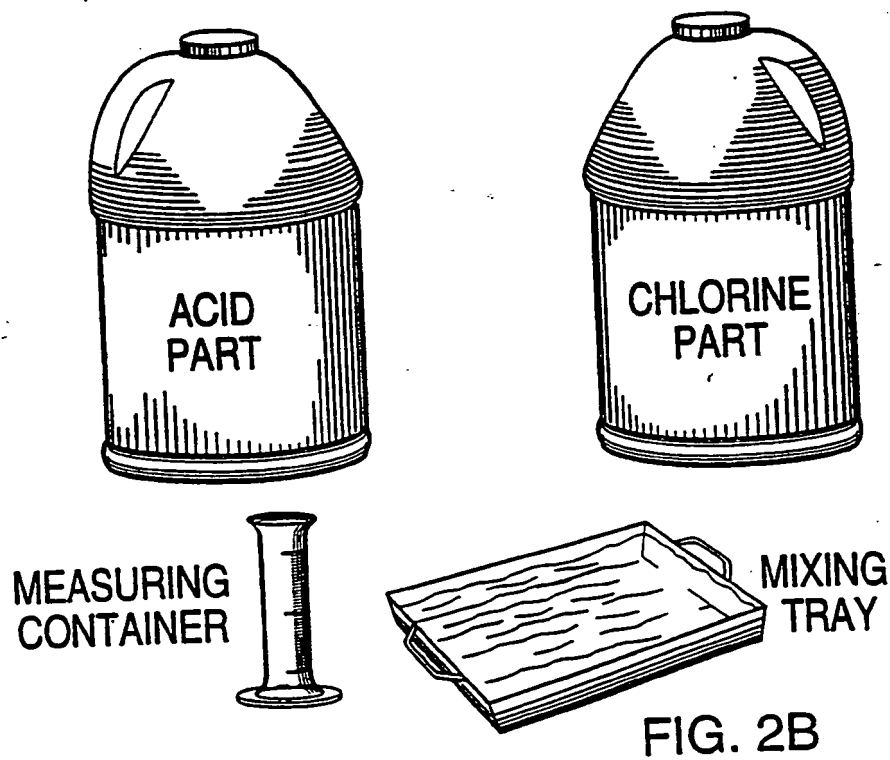
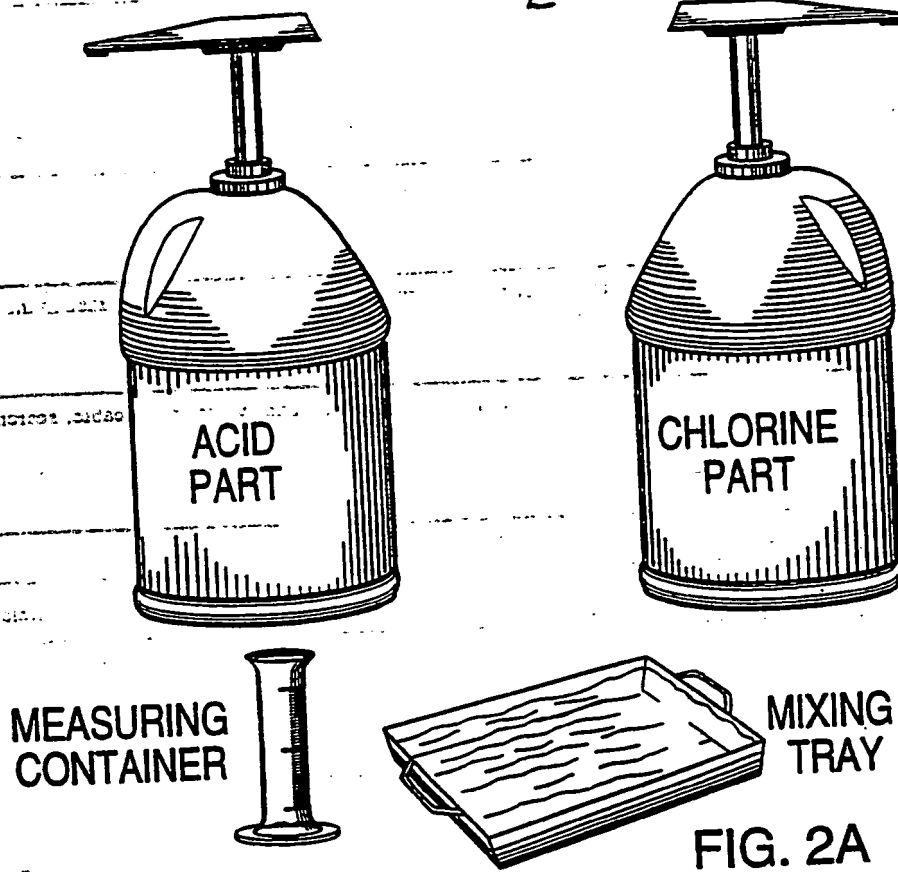


FIG. 1

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## INTERNATIONAL SEARCH REPORT

PCT/US93/02015

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C01B 11/02

US CL :423/477

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/472,473,475,478

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

Searched: Aldehyde and Chlorine dioxide

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO, 85/04107 (DAVIDSON) 26 SEPTEMBER 1985 See page 8, line 9-25, page 4, line 19-26, page 5, lines 1-7, page 6, lines 13-26, page 7, lines 1-10, claims 15,16,24 and 26	1-20
Y	US,A, 2,323,594 (HAMPEL) 06 JULY 1943 See column 1, page 1, lines 25-40	1, 2, 6-20
Y	US,A, 3,386,915 (RUTSCHI) 04 JUNE 1968 See column 1, lines 65-70 and table	1, 3, 4, 10, 11, 16,17

☒ Further documents are listed in the continuation of Box C.☐ See patent family annex.

Special categories of cited documents:	
*A* document defining the general state of the art which is not considered to be part of particular relevance	T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*E* earlier document published on or after the international filing date	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*O* document referring to an oral disclosure, use, exhibition or other means	*Z* document member of the same patent family
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

12 APRIL 1993

Date of mailing of the international search report

11 JUN 1993

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## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO, 88/08823 (MASON) 17 NOVEMBER 1988 See page 6, claim 16	1-6
A	CA,A, 959,238 (CALLERAMA) 17 DECEMBER 1974 See claims 1-5	1-6
A	Chlorine Dioxide Chemistry and Environmental Impact of Oxychlorine compounds, 1979, W.J. MASSCHELEIN, "Reactions with Organic Compounds", page 67.	1-20

DOCUMENTS CONSIDERED TO BE RELEVANT

Category: Origin of document, date of origin, where applicable, of the relevant material

1-2  
W.C. 88-00000 (PERSON)  
See page 6, claim 10

1-4  
A  
17 DECEMBER 1974  
CA, A, 822, 218 (CALLERMAN)  
See claims 1-7

1-20  
A  
Chlorine Dioxide Chemistry and Environmental Impact of  
Oxochlorine compounds, 1979, W.J. MASSCHELEIN, "Research  
with Organic Compounds", page 67.